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*January 10, 2005*

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Under Secretary  
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## PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR  
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### TITLE OF THE INVENTION (500 characters max)

EPOXY-BASED FOAMS

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### ENCLOSED APPLICATION PARTS (check all that apply)

Specification	Number of Pages	16
Drawings	Number of Sheets	1
Abstract	Number of Sheets	1

☒ Applicant Claims Small Entity Status

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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No  
☐ Yes, the name of the Government Agency and the Government Contract Number are:

Respectfully submitted,



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## **EPOXY-BASED FOAMS**

**Inventor: Edward W. Taylor, Jr.**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

Not applicable.

### **STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT**

Not applicable.

### **REFERENCE TO MICROFICHE APPENDIX**

Not applicable.

### **BACKGROUND OF THE INVENTION**

The present invention is directed generally to foams and methods of producing foams and more specifically to methods of producing epoxy-based foams at ambient temperatures and pressures. The invention has particular, but not exclusive, use in the preparation of fire-resistant foams.

Historically, foamed polymeric matrices have been used for insulation of walls, tanks, ceilings, and other structures. They have also been used as structural elements. Certain modified foams have also been used for fire protection. These foams have been made from various materials including urethane, epoxy, polyimides, silicones and the like, which are formed using a process referred to as blowing. Blowing may occur during polymerization, or in a softened polymer. Blowing may be accomplished using either physical or chemical blowing agents.

Physical blowing agents are substances which are themselves gases at the working temperature of the foaming process. They may either be injected as gases or

else change state, typically from liquid to gas at the temperature and pressure of foam production. Chemical blowing agents undergo a chemical reaction (either by decomposition or by reacting with another composition) to generate a gas. The agents come in various forms, each with its own temperature of activation, generally ranging from 105°C - 260°C (232°F - 500°F). General discussions of polymeric foams and their methods of generation are found in the background sections of, for example, Lee et al., U.S. Patent 6,583,190 and Garcia et al., U.S. Patent RE. 35,447, incorporated by reference herein.

Although current physical and chemical blowing techniques have been successfully used to produce foams, a need still exists for other more desirable blowing techniques. Aside from the obvious complexity added by elevated temperatures and the physical dangers they engender, damage to the polymeric material often results. Additionally, high processing temperatures restrict the types of additives used in the foam to give the foam other desirable properties, for example, fire resistance because of premature activation of the additives.

Other methods of blowing foams exist, including frothing. Although frothing can produce a foamed epoxy matrix, control over the process must be strict to avoid under or over frothing, which will result in foam that lacks the desired properties. Frothing can also be used only in a limited number of applications.

Accordingly, a need exists for methods of producing foams that are not labor intensive, and do not require elevated processing temperatures.

## SUMMARY OF THE INVENTION

In accordance with one aspect of the present invention, a method of forming a polymeric foam is provided that includes reacting a sulfonyl hydrazide chemical blowing

agent with a curing agent to form the foam, wherein the curing agent is a water-borne polyamide. In some embodiments, the foam is epoxy based. In some embodiments the polyamide is an emulsion of an adduct of a polyamide. The process is substantially isothermic.

Foams, including epoxy-based foams and other foams, formed by this method are also provided.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph representing the results of a propane test on one embodiment of the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

Unique and reproducible methods of forming stable, epoxy-based foam products have been discovered that are not labor intensive and do not require either elevated processing temperature or reduced pressure. One method comprises reacting at least one sulfonyl hydrazide chemical blowing agent with at least one curing agent at a temperature between 35°F and about 100° F to form the epoxy-based foam, wherein the curing agent is a water-borne polyamide, preferably an emulsion of an adduct of a polyamide. In accordance with the methods described herein, epoxy-based foams may be produced at room temperature, as well as at a wide range of temperatures above and below room temperature, to suit particular applications. As used herein the phrase “room temperature” means in the range of about 15°C to about 30°C (60°F to about 85°F). Accordingly, there is no need for careful temperature control during the curing process, or the use of noxious catalysts or hazardous ingredients. The foams of the invention may be produced at room temperature, as well as temperatures as low as 35°F, with no practical upper limit on temperature other than that imposed by the thermal stability of the polymer. The methods of the invention may also be practiced at normal atmospheric

pressure (approximately 760 torr), or at a wide range of ambient pressures, or at any other convenient pressure to suit the application. Further, the foaming methods of the invention are surprisingly neither exothermic, nor endothermic, but appear to be substantially isothermal. Because of the favorable reaction conditions, the present foaming methods may be conveniently practiced at a job site or in numerous other applications which have been difficult or impossible with presently known foaming methods.

The foams that are produced by the ingredients and by the methods described herein are also within the scope of the present invention. The foams formed may be lightweight, low density, ambient- cured, closed-cell foams that may be used for insulation, protective coatings, as well as for other purposes. The presently preferred foams are epoxy-based, but other binders or resins may be used, for example, an epoxy/polysulfide mixture may be employed, or entirely different binder systems may be employed. It has been found that merely the sulfonyl hydrazide chemical blowing agent and the water-borne polyamide will together form a foam having desirable properties. Therefore, the system may be in principle be utilized with any resin system compatible with these constituents.

The foams may be applied as liquid materials, which then foam under ambient temperatures and pressures, or as solid panels that have been pre-cast and delivered, or formed at the insulation or use site.

The density of the foams produced varies based on many factors, including the amount of blowing agent used, the rate of the curing system, the type of epoxy resin used, the type of curing agent used, the degree of external pressure, the conditions of

polymerization, and the presence and type of fillers used. The rigidity of the foams also varies based on many factors, including the pigment load, types of fillers used, degree of polymerization and degree of cross-linking between the epoxy resins and chemical blowing agents employed. The foams can be applied by any known method of applying foams, including extrusion, casting the foams into molds and hand or spray application.

At least one curing agent must be utilized in the methods of the invention. Due to the nature of the curing mechanism, the foams will cure in 100% humidity and even under water. Among the curing agents that are appropriate for the methods of the invention are water-borne epoxy curing agents that are emulsions of an epoxy adduct, the reaction product of a poly alkylene oxide monoamine or diamine and a diepoxide or a polyepoxide then reacted with a polyamine or a polyamide, or the reaction of a poly alkylene oxide monoalcohol and a polyepoxide, which is then reacted with a polyamine or a polyamide. Examples of suitable curing agents useful in the methods of the invention, include, but are not limited to products available under the trademarks Anquamine® 701, Anquamine® 401, Anquamide® 360, which are all sold by Air Products and Chemicals of Allentown, PA, Epi-Cure 8535®, which is sold by Resolution Performance Products, LLC of Houston, Texas, and Aradur 340®, which is sold by Vantico Group S.A. of Luxembourg. Detailed methods for making useable curing agents are described in Klipstein, U.S. Patent 5,854,312, incorporated by reference herein. These agents may be used alone, or in combination with other suitable curing agents. Other curing agents useful in the methods of the invention will be obvious to those skilled in the art.



Preferably, a total of about 30.0% to about 70.0% of curing agent is used in the methods of the invention. More preferably, a total of about 44.0% to about 56.0% of curing agent is used in the methods of the invention. In one embodiment of the invention, a total of 55.0% of curing agent is employed. In another embodiment of the invention, a total of 44.0% of curing agent is employed. However, the use of concentrations outside of this range is also contemplated.

Any epoxy resin that is capable of cross-linking with the curing agents described herein is suitable for use in the methods of the invention. The resins are added to the foams to improve flexibility and to decrease the hardness of the foams. Suitable epoxy resins include, but are not limited to, Bisphenol A or Bisphenol F liquid epoxy resins. However, the use of concentrations outside of this range is also contemplated.

At least one sulfonyl hydrazide-based chemical blowing agent is employed in the methods of the invention. The chemical blowing agents may be used alone, or in combination. The preferred sulfonyl hydrazide chemical blowing agents are p-toluenesulfonylhydrazide and p,p'-oxybis(benzenesulfonylhydrazide). These are available from Uniroyal, Inc. of Middlebury, CT, under the trademarks Celogen® TSH and Celogen OT®, respectively. It should be noted that other blowing agents may be utilized in the methods of the invention, such as 2,4-toluenedisulfonylhydrazide, p-methylurethane benzene-sulfonyl hydrazide, benzenesulfonylhydrazide, benzene-1,3-disulfonylhydrazide, diphenylsulfone-3,3'-disulfonylhydrazide, and sulfone hydrazide. The blowing agents that are preferred in the compositions and methods of the invention have relatively high activation temperatures which prevent premature activation during compounding. As a result, vapor is produced later in the composite-making process, as

the temperature increases after the matrix resin begins to gel. As a result, the vapor produced on decomposition of the foaming agent is trapped in the resin and, therefore, not released.

Preferably, a total of about 0.01% to about 10.0% of chemical blowing agent is used in the methods of the invention. More preferably, a total of about 8.0% to about 10.0% of chemical blowing agent is used in the methods of the invention. In one embodiment of the invention, a total of 10.0% of chemical blowing agent is employed. In another embodiment of the invention, a total of 8.0% of chemical blowing agent is employed. However, the use of concentrations outside of this range is also contemplated.

In one embodiment of the invention, a fire retardant is introduced into the epoxy-based foam to impart fire resistance to the foam. As used herein, the term "introduced" includes admix, acquaint, bring into physical or reactive contact, insert, add, place among others, insinuate, interpolate, intercalate, interpose and interject. In specific embodiments of the invention, the epoxy foam of the invention may be rendered fire resistant by the introduction of one or more of the following: phosphates, endothermic fillers, char forming agents, tris(hydroxyethyl)isocyanurates and polyfunctional alcohols.

Other additives may also be introduced into the foams of the invention without departing from the spirit and scope of the invention. Those additives include, but are not limited to other resins, colorants and both low and high solubility fillers. Low solubility filler may be introduced to achieve better water resistance. Lower density can be achieved by the introduction of certain lightweight fillers, including glass micro spheres, ceramic micro spheres and Perlite. Lower density may also be achieved by the addition of one or more additional chemical blowing agents.

## EXAMPLES

### EXAMPLE 1

#### Part A

Epoxy Resin	33g
Celogen OT	6.6g
Ammonium Polyphosphate	7.9g
Melamine	3.6g

#### Part B

Anquamine® 701	40g
Titanium Dioxide	5g

Parts A and B were admixed together and placed in a mold on a steel Q-panel with a nominal 2 inches of normal weight concrete poured on the opposite side. A thermocouple was imbedded in the concrete at the surface of the steel to monitor the steel temperature during a fire. Once allowed to foam and cure, the sample was subjected to a small-scale fire. The test was concluded after 75 minutes. The results are shown in Figure 1, Graph 1.

### EXAMPLE 2

34.6% epoxy resin  
55.4% Anquamine® 701  
10.0% Celogen OT

The substances listed above were admixed to produce an epoxy-based foam. The resultant mixture had a wet density equal to 71.35 lbs/cu. Ft., dry density equal to 18.29 lbs/ cu. Ft. and a compressive strength 10% yield equal to 926 psi.

### EXAMPLE 3

27.7% epoxy resin  
44.3% Anquamine® 701  
8.0% Celogen ®OT  
5.0% Ammonium Polyphosphate  
5.0% Melamine  
5.0% Dipentaerithritol  
5.0% Melamine Pyrophosphate

The substances listed above were admixed to produce an epoxy-based foam. The foam was then subject to a two-minute propane test, whereby the foam was subject to an 800°C flame. Prior to the propane test, the original weight was 5.630 grams, the thickness was .458 inches and the density was 17.69 lbs/cu. Ft. After the propane test, the foam weighed 4.856 grams, had a char height of 1.008 inches and a thickness (of the remaining foam) of .434 inches. 94.76% of the foam remained after the propane test and the expansion from the used foam was 42x.

What is claimed:

1. A method of forming a foam, the method comprising reacting at least one sulfonyl hydrazide chemical blowing agent with at least one curing agent to form the foam, wherein the curing agent is a water-borne polyamide.
2. The method of claim 1 wherein the reaction occurs at about 35°F.
3. The method of claim 1 wherein about .01% to about 10.0% of said sulfonyl hydrazide is reacted with the at least one curing agent.
4. The method of claim 1 wherein about 8.0% to about 10.0% of said sulfonyl hydrazide is reacted with the at least one curing agent.
5. The method of claim 1 wherein about 10% of said sulfonyl hydrazide is reacted with the at least one curing agent.
6. The method of claim 1 further comprising introducing at least one fire retardant into the foam.
7. The method of claim 6 wherein said fire retardant is at least one selected from the group consisting of phosphates, endothermic fillers, char forming agents, tris(hydroxyethyl)isocyanurates and polyfunctional alcohols.
8. The method of claim 1 further comprising reacting at least one epoxy resin with the at least one sulfonyl hydrazide.
9. The method of claim 8 wherein said epoxy resin is a bis-phenol A type epoxy resin.
10. The method of claim 8 wherein said epoxy resin is a bis-phenol F type epoxy resin.

11. The method of claim 8 wherein about 25.0% to about 70.0% of said at least one epoxy resin is introduced into the reaction.
12. The method of claim 8 wherein about 28.0% to about 35.0% of said at least one epoxy resin is introduced into the reaction.
13. The method of claim 8 wherein about 35.0% of said at least one epoxy resin is introduced into the reaction.
14. The method of claim 8 wherein about 28.0% of said at least one epoxy resin is introduced into the reaction.
15. The method of claim 6 wherein about 8.0% of said at least one sulfonyl hydrazide chemical blowing agent is reacted with the at least one curing agent.
16. The method of claim 1 wherein about 30.0% to about 70.0% of said at least one curing agent is reacted with the at least one sulfonyl hydrazide chemical blowing agent.
17. The method of claim 1 wherein about 44.0% to about 56.0% of said at least one curing agent is reacted with the at least one sulfonyl hydrazide chemical blowing agent.
18. The method of claim 1 wherein about 55.0% of said at least one curing agent is reacted with the at least one sulfonyl hydrazide chemical blowing agent.
19. The method of claim 6 wherein about 44.0% of said at least one curing agent is reacted with the at least one sulfonyl hydrazide chemical blowing agent.
20. The method of claim 1 wherein said at least one chemical blowing agent is p-toluenesulfonylhydrazide.

21. The method of claim 1 wherein said at least one chemical blowing agent is p,p'-Oxybis(benzenesulfonylhydrazide).
22. The method of claim 1 further comprising introducing at least one low-density filler into the epoxy-based foam.
23. A method of forming an epoxy-based foam, the method comprising reacting at least one of p-toluenesulfonylhydrazide and p,p'-oxybis(benzenesulfonylhydrazide) with at least one curing agent, and at least one epoxy resin at a temperature between room temperature and about 100° F to form the epoxy-based foam, wherein the curing agent is an emulsion of an adduct of a polyamide.
24. A method of forming an epoxy-based foam, the method comprising reacting at least one of p-toluenesulfonylhydrazide and p,p'-oxybis(benzenesulfonylhydrazide) with at least one curing agent, at a temperature between room temperature and about 100° F to form the epoxy-based foam, and introducing at least one fire retardant into the epoxy based foam, wherein the curing agent is an emulsion of an adduct of a polyamide, and the epoxy resin is capable of cross-linking with the at least one curing agent.
25. A foam produced by the method of claim 1.
26. The foam of claim 25 wherein the foam comprises an epoxy or modified epoxy resin.
27. The epoxy-based foam of claim 25 wherein the foam produced is cast.
28. A fire resistant foam produced by the method of claim 6.
29. The foam of claim 28 wherein the foam comprises an epoxy or modified epoxy resin.
30. The epoxy-based foam of claim 29 wherein the foam is applied as a protective coating on a substrate.

31. A foam comprising at least one sulfonyl hydrazide chemical blowing agent and at least one curing agent, wherein the curing agent is an emulsion of an adduct of a polyamide.
32. The foam of claim 31 further comprising an epoxy resin.
33. The foam of claim 31 where said at least one sulfonyl hydrazide chemical blowing agent is p-toluenesulfonylhydrazide.
34. The foam of claim 31 where said at least one sulfonyl hydrazide chemical blowing agent is p,p'-oxybis(benzenesulfonylhydrazide).
35. The epoxy-based foam of claim 32 wherein the epoxy resin is a Bisphenol A type resin.
36. The epoxy-based foam of claim 32 wherein the epoxy resin is a Bisphenol F type resin.
37. The epoxy-based foam of claim 32 further comprising at least one fire retardant.
38. The foam of claim 31 wherein said foam is applied to a substrate as a coating.
39. The foam of claim 31 wherein said foam is solid.
40. The epoxy-based foam of claim 37 wherein said fire retardant is at least one selected from the group consisting of phosphates, endothermic fillers, char forming agents, tris(hydroxyethyl)isocyanurates and polyfunctional alcohols.
41. The epoxy-based foam of claim 32 comprising about .01% to about 10.0% of said sulfonyl hydrazide chemical blowing agent.



42. The epoxy-based foam of claim 32 comprising about 8.0% to about 10.0% of said sulfonyl hydrazide chemical blowing agent.
43. The epoxy-based foam of claim 32 comprising about 10% of said sulfonyl hydrazide chemical blowing agent.
44. The epoxy-based foam of claim 32 comprising about 25.0% to about 70.0% of said at least one epoxy resin.
45. The epoxy-based foam of claim 32 comprising about 28.0% to about 35.0% of said at least one epoxy resin.
46. The epoxy-based foam of claim 32 comprising about 35.0% of said at least one epoxy resin.
47. The epoxy-based foam of claim 32 comprising about 28.0% of said at least one epoxy resin.
48. The epoxy-based foam of claim 31 comprising about 30.0% to about 70.0% of said at least one curing agent.
49. The epoxy-based foam of claim 31 comprising about 44.0% to about 56.0% of said at least one curing.
50. The epoxy-based foam of claim 31 comprising about 55.0% of said at least one curing agent.
51. The epoxy-based foam of claim 31 comprising about 44.0% of said at least one curing agent.

52. An epoxy-based foam comprising at least one of p-toluenesulfonylhydrazide or p, p'-oxybis(benzenesulfonylhydrazide) and at least one curing agent, wherein the curing agent is an emulsion of an adduct of a polyamide.

53. An epoxy-based foam comprising:

at least one of p-toluenesulfonylhydrazide or p, p'-

oxybis(benzenesulfonylhydrazide);

at least one epoxy resin; and

at least one curing agent, wherein the curing agent is an emulsion of an adduct of a polyamide.

54. A foam comprising the reaction product of a sulfonyl hydrazide and a water-borne polyamide.

55. The foam of claim 54 wherein the water-borne polyamide is an emulsion of an adduct of a polyamide.

55. A chemical blowing agent comprising a sulfonyl hydrazide and a water-borne polyamide.

56. A method of forming a polymeric foam comprising reacting a sulfonyl hydrazide and a water-borne polyamide at generally ambient temperature and generally ambient pressure.

57. The method of claim 56 wherein the polyamide comprises an emulsion of an adduct of a second polyamide.

## ABSTRACT OF THE DISCLOSURE

Methods of forming epoxy-based foams are described that include reacting at least one sulfonyl hydrazide chemical blowing agent with at least one curing agent at a temperature between 35°F and about 100° F. Generally, the curing agent is an emulsion of an adduct of a polyamide.

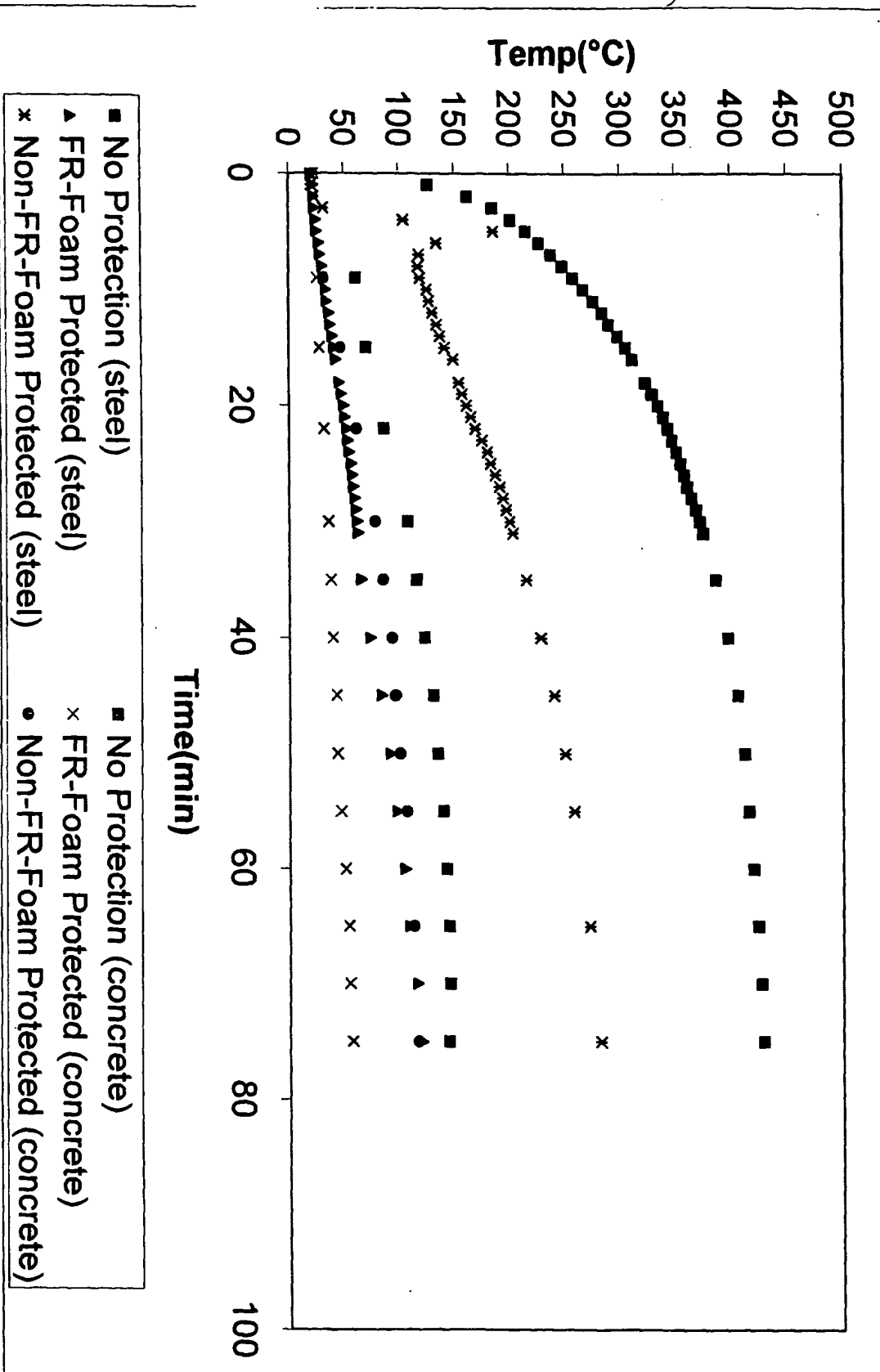


FIGURE 1

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